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A simple route to derivatives of benzo[*j*]fluoranthene

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ABSTRACT

3,6,8,11-Tetramethoxybenzo[*j*]fluoranthene can be made from 1,6-dimethoxynaphthalene in a one-pot ferric chloride oxidation/methanol reduction procedure. The reaction is tolerant of the presence of substituents in the 7-position of the naphthalene nucleus and provides a quick and easy route to these particular benzo[*j*]fluoranthenes. The reactions presumably proceed through initial formation of a bond between the 4-positions of two naphthalene molecules followed by closure of the five-membered ring. Indeed in one case some 4,4′-binaphthyl was isolated from the reaction mixture and it was generally found that better yields of the benzo[*j*]fluoranthrenes were obtained starting from the 4,4′-binaphthyl rather than by using the naphthalene as the starting material. In an analogous manner to the ring-closure of the 4,4′-binaphthyls, starting from a hexakisalkoxyphenylnaphthalene, a hexakisalkoxyfluoranthene could be obtained.

1. Introduction

Studies of the mechanism of aryl–aryl oxidative coupling show that, under strongly oxidizing conditions, what is finally produced is very often a solution of the radical cation[1] or polycation[2] of the desired product, which has to be reduced back to the neutral molecule. This understanding underlays the development of a two-step version of the Scholl reaction, in which excess ferric chloride in dichloromethane is used as the oxidant in the usual way, but the reaction mixture is worked up reductively with methanol.[3] This protocol has mainly been used in the liquid crystal field where it has proved important in the synthesis of alkoxy substituted biphenyls[4] (dimerization of benzene derivatives), symmetrically substituted triphenylenes (trimerization of benzene derivatives),[5] unsymmetrically substituted triphenylenes (regiospecific cross-coupling of benzene and biphenyl derivatives)[6] and systems with more extended polynuclear aromatic cores (mostly examples of variants of the *ortho*-terphenyl to triphenylene reaction).[7] Variants have been introduced using vanadium oxychloride,[8] molybdenum(V) chloride,[9] ferric chloride/alumina[10] or ferric chloride/nitromethane[11] as the oxidant. Methoxy and most primary alkoxy substituents survive these reaction conditions but *iso*-propoxy substituents are cleaved (probably during the methanol workup) allowing phenols to be obtained directly from this one-pot process; despite the strongly oxidizing nature of first step.[12] Very high yields can be obtained but this is dependent on the use of an excess of the oxidant, the use of a non-nucleophilic solvent and the use of a reductive, non-aqueous workup. Aqueous solvents and aqueous workups usually result in mixtures of ring-hydroxylation products and quinones, both of which arise ultimately from attack of water on cationic intermediates. Although strong acids (most often TFA or sulfuric acid) have sometimes been added to the reaction medium to suppress dealkylation,[5b,12] this is unnecessary since the mixture rapidly becomes highly acidic through the HCl that is evolved.

2. Results and discussion

In the search for new applications for this protocol we investigated the oxidative dimerization of a variety of methoxynaphthalene derivatives and were surprised to find that 1,6-dimethoxynaphthalene **1a** (Scheme 1) gave a bright yellow crystalline 'dimer' [$C_{20}H_8(OMe)_4$] showing three aromatic methoxy signals (6H,3H,3H) in the ^{1}H NMR spectrum together with two 1H singlets and six 1H doublets between δ 6.7 and 8.2. A single crystal X-ray crystallographic study showed this product to be 3,6,8,11-tetramethoxybenzo[*j*]fluoranthene **2a** (Fig 1).

Although the yield obtained from dimethoxynaphthalene was not high (up to 45% after chromatography and recrystallization and using an optimized 6–8 M equiv of ferric chloride) this reaction provides a very simple entry to some unusual benzo[*j*]fluoranthene derivatives. In general, although there are many convenient routes to benzo[*j*]fluoranthene itself,[13] those for ring-substituted

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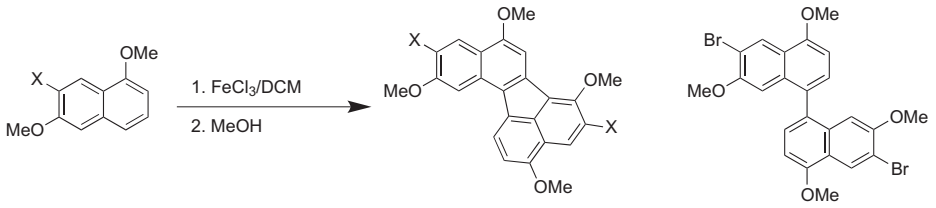


1a) X = H
1b) X = I
1c) X = Br
1d) X = C_6H_4OMe
1e) X = OMe

2a) X = H, 30-45%
2b) X = I, 0%
2c) X = Br, 25%
2d) X = C_6H_4OMe, 0%
2e) X = OMe, 42-65%

3), 60%

Scheme 1. Oxidative dimerization of derivatives of 1,6-dimethoxynaphthalene.

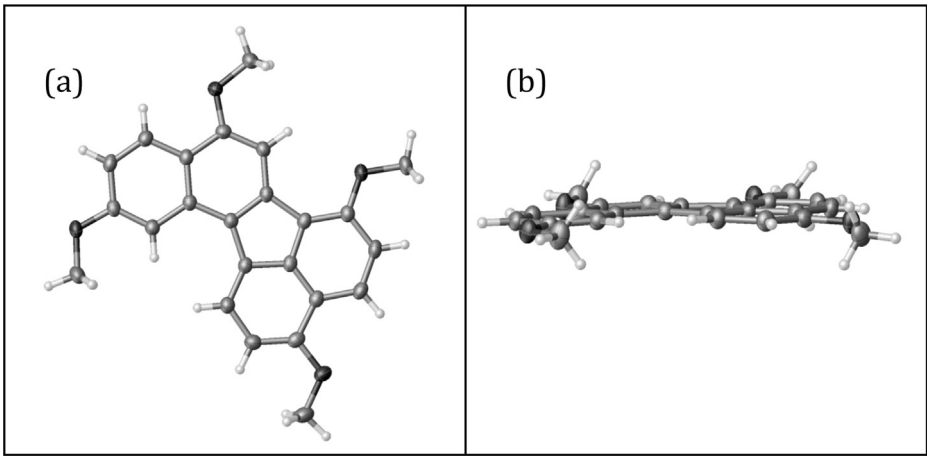


Fig. 1. (a) X-ray crystallographic structure of 3,6,8,11-tetramethoxybenzo[*j*]fluoranthene **2a** (solvent molecules omitted for clarity, atomic displacement parameters drawn at 50% probability) (b) Structure rotated to display the planar nature of the aromatic core. C: dark grey, O: black, H: light grey.

derivatives often involve many steps.[13c,14] In an attempt to extend the scope of the synthesis we have investigated a series of 7-substituted derivatives of 1,6-dimethoxynaphthalene and the results of these studies are summarized in Scheme 1.

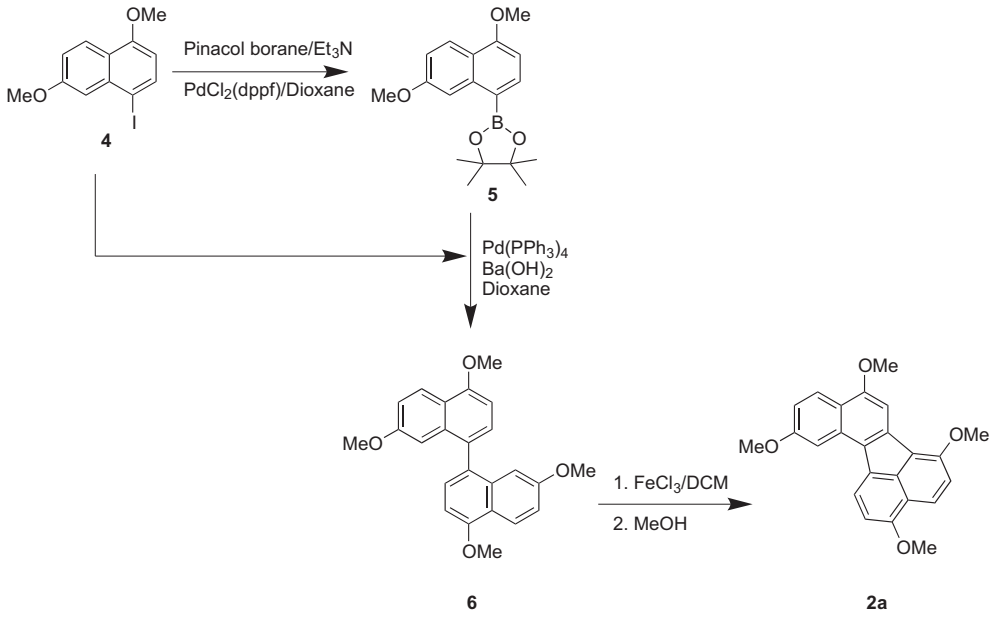
In terms of the starting materials used in this study, the 7-iodonaphthalene **1b** is readily obtained by regiospecific lithiation of 1,6-dimethoxynaphthalene at −78 °C followed by a workup with iodine using the method of Mellin and Hacksell.[15] This was converted to the bromide **1c** by reaction with cuprous bromide[16] and to the *para*-methoxyphenyl derivative **1e** through a Suzuki reaction.[17] The trimethoxynaphthalene **1e** was obtained through a Diels–Alder reaction between 4,5-dimethoxybenzyne and furan,[18,19] acid catalyzed ring opening of the adduct to give 6,7-dimethoxynaphthol and methylation using methyl iodide/potassium carbonate.

The iodo-derivative **1b** did not survive the rather strong ferric chloride oxidative reaction conditions and neither did the methoxyphenyl system **1d**. However, the methoxy derivative **1e** gave the corresponding 'dimer' in reasonably good yield (up to 65%) and as a single regioisomer, whilst the bromo derivative **1c** gave a more modest yield (~25%).

It seems likely that the regiospecificity of these reactions is dictated by the fact that the first carbon–carbon bond formed is between the 4-positions of two naphthalene molecules:[20] possibly a 4,4-coupling of a pair of radical cations. In support of this hypothesis we were able to show that the putative intermediate **6** in the 'dimerization' of **1a** gives a higher yield of **2a** (65%) than that obtained directly from **1a** under identical reaction conditions (Scheme 2). The 4-iodonaphthalene **4** was made by reacting 1,6-dimethoxynaphthalene with *N*-iodosuccinimide and catalytic TFA (78%),[21] converted to the boronic ester **5** by a palladium mediated reaction with pinacol borane (84%) and the binaphthyl **6** obtained by coupling **4** and **5** under standard Suzuki conditions (89%). Perhaps the most persuasive evidence for the idea that 4,4′-binaphthyl intermediates are involved in these reactions is that the major product (~60%) in the attempted dimerization of **1c**, is in fact the corresponding 4,4′-binaphthyl **3** (Scheme 1). Indeed, we attribute the low yield of **2c** via the direct dimerization of **1c** to the limited solubility of the intermediate **3** and, in particular, of its carbocation.

A rather unusual aspect of the dimerization reactions shown in Scheme 1 is that oxidative couplings of this type usually result in bond formation '*ortho*' or '*para*' to alkoxy or alkylamino substituents (bond formation at the sites where the spin-density of the radical cation intermediates is highest) but, in the benzo[*j*]fluoranthene forming reactions, one of the bonds is formed '*meta*' to an alkoxy group. However, if the binaphthyl shown in Scheme 2 is indeed an intermediate then the '*meta*' coupling (coupling *o*–*m* shown in formula **6**) follows naturally because '*ortho*' coupling (coupling *o*–*o* in formula **6**) would lead to a very sterically hindered product.

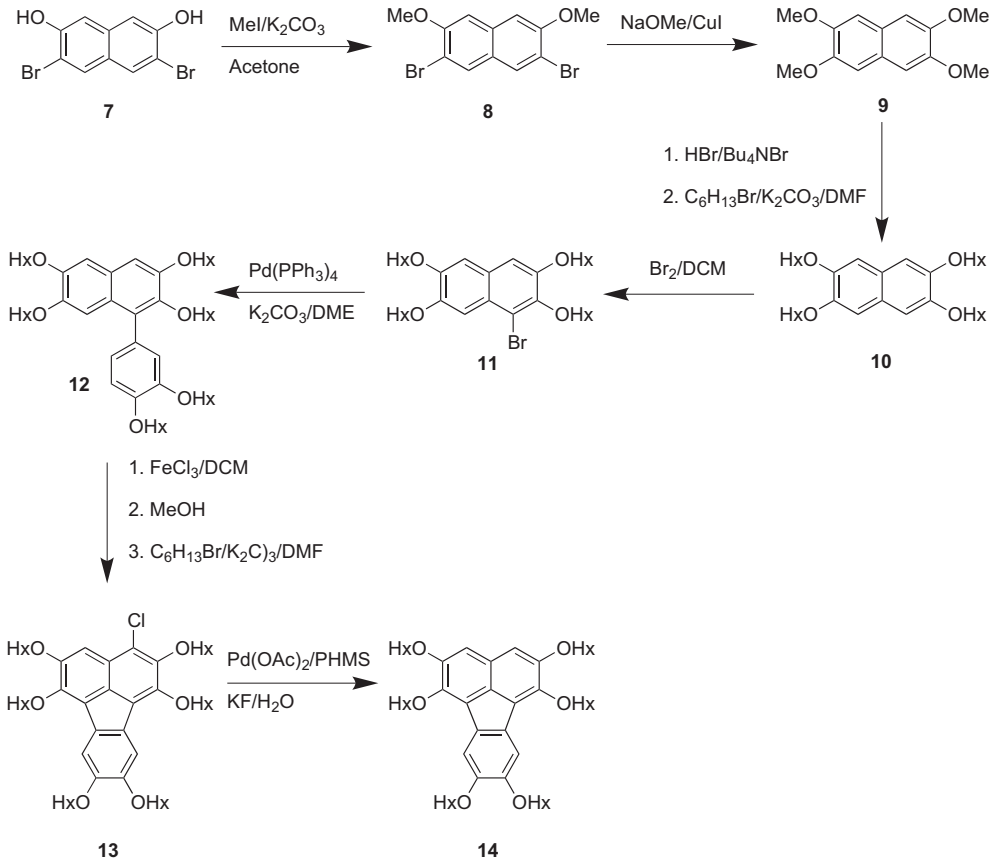
Since these reaction conditions were effective in the formation of fused naphthyl/five-membered ring products; we next addressed the possibility of using this approach for the synthesis of fluoranthenes through the cyclization of 1-phenylnaphthalenes. The target molecule chosen was compound **14** (Scheme 3). This was chosen because (1) oxidative coupling reactions of this type generally are best for polyalkoxylated aromatic compounds; (2) in the intermediate phenylnaphthalene **12** there is a sterically unhindered



Scheme 2. Synthesis of the benzo[*j*]fluoranthene **2a** by oxidative cyclization of the binaphthyl.

'*ortho*/*para*' (high spin site to high spin site) coupling; (3) this coupling (*o*–*p* in formula **12**) gives a less sterically hindered product than the alternative (*o*–*o* in formula **12**) and so the reaction should be regiospecific; and (4) it was hoped that the product **14**, like the triphenylene derivative 2,3,6,7,10,11-hexahexyloxytriphenylene,[22] would be liquid crystalline.

The first part of the synthesis shown in Scheme 3 was based on the route to 2,3,6,7-tetramethoxynaphthalene **9** described by Hellberg et al.[23] although some modifications were required. Hence, 2,7-dihydroxynaphthalene was treated with excess bromine and the polybrominated intermediate(s) reduced back to 3,6-dibromo-2,7-dihydroxynaphthalene **7** with tin in a simple one-



Scheme 3. Synthesis of the fluoranthene **14** through oxidative cyclization of the phenylnaphthylene.

pot procedure. Alkylation with methyl iodide to give 3,6-dibromo-2,7-dimethoxynaphthalene **8** was straightforward but attempts to prepare 2,3,6,7-tetramethoxynaphthalene from this according to the procedure of Hellberg et al. using stoichiometric amounts of sodium methoxide and copper(I)iodide were met with very little success. However, when excess sodium methoxide was used and additional copper(I)iodide was added during the reaction, a 70% yield was obtained. The problem is most likely related to the ease with which copper(I) catalysts degrade under the reaction conditions.[24] Conversion to 2,3,6,7-tetrakis(hexyloxy)naphthalene **10** was achieved by dealkylation using HBr/Bu_4NBr to give the air-sensitive tetrahydroxynaphthalene, which was not isolated but immediately realkylated using hexylbromide/potassium carbonate. Monobromination and a Suzuki coupling reaction gave the desired phenylnaphthalene **12** without difficulty. As sometimes happens with long-chain alkoxy ethers under ferric chloride/methanol coupling conditions, the oxidative cyclization of **12** was accompanied by a small amount of dealkylation. The ease/extent of dealkylation in these ferric chloride mediated couplings usually increases methoxy<<other primary alkoxy<<secondary alkoxy. In this case the TLC of the crude product showed several yellow 'fluoranthene spots' and so the crude reaction mixture was realkylated using hexylbromide/potassium carbonate,[25] which gave a single major product (one yellow 'fluoranthene spot' in the TLC). However, this was not the expected product **14** but the monochloro compound **13** (accurate mass for $C_{52}H_{81}O_6Cl$ and 1H singlets at δ 7.68, 7.62 and 7.21 in the ^1H NMR spectrum). Although this type of ring chlorination under ferric chloride/dichloromethane coupling conditions is very unusual it is not without precedent.[26] The 3-chloro (rather than 7-chloro) structure for compound **13** is somewhat tentatively assigned on the basis of the aromatic chemical shifts and likely steric hindrance in the case of 7-chloro. Attempts to confirm the structure by means of 2-D HSQC and HMBC experiments proved inconclusive. Reduction of **13** to **14** using $Pd(OAc)_2$/PHMS/KF[27] gave a 63% yield of the desired product **14**. This was obtained as a low-melting yellow solid (mp. 33 °C) and showed no liquid crystal properties.

3. Conclusions

Most interest in benzo[*j*]fluoranthene and its derivatives arises because of their carcinogenic activity and the fact that they are so widely spread in the environment.[28] However, benzofluoranthenes also have unique electro-optic properties, which are suggestive of potential applications.[29] We have shown that tetraalkoxy benzo[*j*]fluoranthenes can be made in a very simple manner by oxidative dimerization of 1,6-dialkoxynaphthalenes. We propose that the reaction proceeds through a binaphthyl intermediate followed by closure of the five-membered ring. In suitable cases, alkoxylated benzo[*j*]fluoranthenes can also be made from the corresponding binaphthyls or fluoranthenes from the corresponding alkoxylated phenylnaphthalenes.

4. Experimental section

4.1. General procedures

Unless otherwise stated, all reagents and solvents were obtained from commercial suppliers and were used without further purification. Anhydrous THF, diethyl ether, dioxane and toluene were pre-dried over sodium wire prior to continuous distillation over sodium-benzophenone (except toluene, which was distilled over sodium). DCM was pre-dried over calcium chloride and freshly distilled over calcium hydride. All were distilled under an atmosphere of oxygen free molecular nitrogen. Other anhydrous solvents were used as supplied (water content <0.05%). ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a 300 or 500 MHz spectrometer. The progress of reactions was monitored by TLC on pre-coated silica plates and visualized by ultraviolet light or staining with vanillin or potassium permanganate. Column chromatography employed Merck Kieselgel (60 Å) F_{254} (230–400 mesh) silica and HPLC grade solvents.

4.2. 7-Iodo-1,6-dimethoxynaphthalene (1b)[15]

Butyllithium (2.5 M solution in hexanes, 10.1 mL, 26.5 mmol) was added dropwise to a cooled (−78 °C) stirred solution of 1,6-dimethoxynaphthalene (5.00 g, 26.5 mmol) in anhydrous THF (50 mL) under an argon atmosphere. Upon completion of the addition, the reaction mixture was allowed to warm to room temperature for 12–14 h. The mixture was again cooled (−78 °C) and iodine (6.74 g, 26.5 mmol) in anhydrous THF (50 mL) was added dropwise over 1 h. The reaction mixture was brought to room temperature and quenched with satd NH_4Cl (10 mL) and satd $Na_2S_2O_3$ (15 mL). The mixture was concentrated in vacuo and the organic dissolved in diethyl ether (200 mL), washed with water (3×50 mL), dried ($MgSO_4$) and concentrated in vacuo to approximately 50 mL. The concentrated solution was filtered through a Celite/silica plug eluting with diethyl ether and the filtrate concentrated in vacuo to yield a colourless solid (6.37 g, 76%), which was recrystallized from MeOH to afford the title compound as off white prisms, mp 110–112 °C (lit.[15] mp 110.5–112 °C). ^1H NMR (300 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.45–7.28 (m, 2H), 7.01 (s, 1H), 6.72–6.54 (d, J=7.6 Hz, 1H) 3.95 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.6, 154.6, 135.6, 134.0, 127.3, 122.2, 119.0, 105.3, 102.5, 86.8, 56.3, 55.5. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 2959, 2928, 2836, 1576, 1447, 1424, 1385, 1359. HRMS (EI^+, 70 eV) m/z: $[M]^+$ calcd for $C_{12}H_{11}O_2I$ 313.9798, found 313.9794. Anal. Calcd for $C_{12}H_{11}O_2I$: C, 45.88; H, 3.53; I, 40.40. Found: C, 46.04; H, 3.26; I, 39.99.

4.3. 7-Bromo-1,6-dimethoxynaphthalene (1c)

7-Iodo-1,6-dimethoxynaphthalene (2.00 g, 6.37 mmol) and copper(I)bromide (1.83 g, 12.7 mmol) were stirred at reflux in anhydrous DMF (30 mL) under an atmosphere of argon for 24 h. The reaction mixture was allowed to cool, diluted with DCM (50 mL) and washed with 10% HCl (3×20 mL), water (2×20 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude brown solid was purified by column chromatography eluting with 20% DCM/hexane v/v ($R_f \approx 0.35$) to yield a colourless powder (1.51 g, 88%), which was recrystallized from EtOH to afford the title compound as colourless plates. Mp 108–110 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.39–7.26 (m, 2H), 7.10 (s, 1H), 6.69 (d, J=6.8 Hz, 1H), 3.99 (s, 3H), 3.97 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.7, 154.0, 134.7, 127.53, 127.47, 121.3, 118.9, 112.3, 106.4, 102.6, 56.2, 55.5. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 3010, 2931, 2836, 1581, 1448, 1427, 1386. HRMS (ESI^+); m/z: $[M+H]^+$ calcd for $C_{12}H_{12}BrO_2$ 267.0015, found 267.0021. Anal. Calcd for $C_{12}H_{11}O_2Br$: C, 53.96; H, 4.15; Br, 29.91. Found: C, 53.70; H, 4.30; Br, 29.85.

4.4. 1,6-Dimethoxy-7-(4-methoxyphenyl)-naphthalene (1d)

Barium hydroxide octahydrate (0.60 g, 1.7 mmol) and $PdCl_2$(dppf) (0.06 g, 0.08 mmol) were added to an argon degassed solution of 7-iodo-1,6-dimethoxynaphthalene (0.50 g, 1.6 mmol) and 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (0.45 g, 1.9 mmol) dissolved in DME/water (60/15 mL) and degassed with argon for a further 1 h. The mixture was brought to reflux for 16 h, allowed to cool, diluted with DCM (100 mL), filtered through a Celite plug. The organics were washed successively with 10% HCl (2×20 mL), water (2×20 mL), dried ($MgSO_4$) and concentrated to afford the crude as a brown oil. This was purified by

column chromatography eluting with 25% DCM/hexane v/v ($R_f \approx 0.35$) to afford a colourless powder (0.40 g, 85%), which was recrystallized from EtOH to afford the title compound as fine colourless needles. Mp 136.5–137 °C. ^{1}H NMR (300 MHz) $CDCl_3$) δ 8.16 (s, 1H), 7.58, (d, J=8.5 Hz, 2H), 7.36 (d, J=4.3 Hz, 2H), 7.18 (s, 1H), 6.99 (d, J=8.5 Hz, 2H), 6.72 (t, J=4.3 Hz, 1H), 3.98 (s, 3H), 3.92 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 155.8, 155.7, 135.1, 131.1, 131.0, 130.9, 126.4, 124.1, 120.7, 118.3, 113.5, 105.5, 102.2, 55.51, 55.47, 55.3. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 3000, 2960, 2936, 2836, 1493. HRMS (EI^+, 70 eV); m/z: $[M]^+$ calcd for $C_{19}H_{18}O_3$ 294.1250, found 294.1246. Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.44; H, 6.10.

4.5. 1,6,7-Trimethoxynaphthalene (1e)

6,7-Dimethoxynaphthol[19] (750 mg, 3.68 mmol), potassium carbonate (761 mg, 5.50 mmol) and methyl iodide (343 μL, 5.50 mmol) dissolved in anhydrous DMF (10 mL) were stirred at 0° C for 2 h under argon. The reaction mixture was diluted with water (10 mL) and extracted with DCM (2×10 mL), washed with brine (10 mL), water (10 mL), dried ($MgSO_4$) and concentrated in vacuo. The resultant crude mixture was purified by column chromatography eluting with 30% EtOAc/hexane v/v ($R_f \approx 0.4$) to yield a colourless powder (742 mg, 91%), which was recrystallized from toluene to afford the title compound as colourless prisms. Mp 133–134 °C (lit.[30] mp 132–133 °C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.31–7.23 (m, 2H), 7.01 (s, 1H), 6.73 (dd, J=7.0, 1.6 Hz, 1H), 4.02 (s, 3H), 4.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9 and 150.1, 149.3, 130.7, 124.9, 121.0, 119.3, 106.6, 103.1, 101.3, 56.3, 56.2 and 55.9. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 3053, 3010, 2961, 2835, 1586, 1500, 1456, 1377. HRMS (EI^+, 70 eV); m/z: $[M]^+$ calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0953. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.35; H, 6.56.

4.6. 3,6,8,11-Tetramethoxybenzo[*j*]fluoranthene (2a)

(a) *From the naphthalene*. Ferric chloride (5.60 g, 34.5 mmol) was added portionwise to a cooled (0 °C) stirred solution of 1,6-dimethoxynaphthalene (1.00 g, 5.3 mmol) dissolved in anhydrous DCM (10 mL) under an atmosphere of argon. Upon completion of the addition the mixture turned deep red/brown in colour and stirring was continued for a further 12 h. The reaction was cooled (0 °C) and quenched with cold methanol (50 mL). The resultant crude was extracted with DCM (100 mL), washed successively with 10% HCl (2×30 mL), water (2×30 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude was purified by column chromatography, eluting with DCM ($R_f \approx 0.30$) to afford a yellow powder (0.44 g, 45%), which was recrystallized from DCM/EtOH. Mp 239 °C. (b) *From the binaphthyl*. Ferric chloride (0.97 g, 6.01 mmol) was added portionwise to a stirred solution of 4,7,4′,7′-tetramethoxy-[1,1′] binaphthalenyl (0.75 g, 2.00 mmol) dissolved in anhydrous DCM (10 mL) under an argon atmosphere. Upon completion of the addition the mixture turned deep red in colour and stirring was continued for 12 h. The reaction was cooled and quenched with cold methanol (30 mL). Workup as before gave a yellow powder (0.47 g, 65%), which was recrystallized from DCM/EtOH. Mp 239–242 °C. ^{1}H NMR (300 MHz $CDCl_3$) δ 8.24 (d, J=9.2 Hz, 1H), 8.15–8.11 (2×d, J=9.2, 7.7 Hz, 2H), 7.86 (d, J=2.1 Hz, 1H), 7.62 (s, 1H), 7.28 (d, J=9.2 Hz, 1H), 7.09 (dd, J=9.2, 2.1 Hz, 1H), 6.79 (d, J=7.7 Hz, 1H), 4.18 (s, 3H), 4.13 (s, 3H), 4.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 156.0, 155.9, 155.2, 137.6, 134.9, 131.8, 130.0, 125.1, 125.0, 123.8, 120.8, 117.7, 115.7, 113.4, 103.9, 103.3, 100.3, 56.0, 55.8, 55.3. HRMS (ESI^+); m/z: $[M+H]^+$ calcd for $C_{24}H_{21}O_4$ 373.1434, found 373.1424. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 2991, 2936, 2838, 1614, 1587, 1480, 1454. Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.42; H, 5.41. Found: C, 77.25; H, 5.75.

4.7. Attempted synthesis of 2b

Compound **1b** was treated in an identical manner to that of **1a**. After extraction and concentration in vacuo, TLC and NMR spectroscopy of the crude product indicated that the desired product was not present.

4.8. 5,10-Dibromo-3,6,8,11-tetramethoxybenzo[*j*]fluoranthene (2c) and 6,6′-dibromo-4,4′,7,7′-tetramethoxy-1,1′-binaphthalene (3)

Anhydrous ferric chloride (1.26 g, 7.87 mmol) was added portionwise to a cooled (0 °C) stirred solution of 7-bromo-1,6-dimethoxynaphthalene (0.30 g, 1.1 mmol) dissolved in anhydrous DCM (5 mL) under an argon atmosphere. The mixture was allowed to warm to room temperature and stirring continued for a further 12 h. Upon completion the mixture was cooled (0 °C) and quenched with cold (0 °C) methanol (20 mL). The mixture was diluted with DCM (50 mL), washed successively with 10% HCl (2×25 mL), water (2×25 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude brown solid was purified by column chromatography eluting with 20% EtOAc/hexane v/v ($R_f \approx 0.60$) to afford **3** (757 mg, 61%) as a colourless solid, which was recrystallized from $CHCl_3$/EtOH. Mp >270 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (s, 2H), 7.36 (d, J=7.9 Hz, 2H), 6.83 (d, J=7.9 Hz, 2H), 6.70 (s, 2H), 4.07 (s, 6H), 3.56 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 154.1, 134.1, 129.2, 127.3, 121.4, 112.6, 105.6, 102.6, 56.0, 55.6; HRMS (EI^+, 70 eV); m/z $[M]^+$ calcd for $C_{24}H_{20}O_4Br_2$ 529.9728, found 529.9722. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 2960, 2932, 2832, 1612, 1586, 1447, 1427, 1317. Anal. Calcd for $C_{24}H_{20}Br_2O_4$: C, 54.16; H, 3.79; Br, 30.03. Found: C, 54.4; H, 3.75; Br, 29.80. Later fractions ($R_f \approx 0.45$) contained compound **2c** as a bright orange solid (312 mg, 25%), which was recrystallized from toluene/EtOH to afford bright orange needles. Mp 242–246 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.39 (s, 1H), 8.03 (d, J=7.7 Hz, 1H), 7.77 (s, 1H), 7.54 (s, 1H), 6.84 (d, J=8.1 Hz, 1H), 4.15 (s, 3H), 4.14 (s, 3H), 4.12 (s, 3H), 4.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 155.5, 154.8, 154.5, 152.6, 136.4, 134.3, 130.5, 129.8, 128.4, 128.0, 127.8, 125.5, 123.9, 121.5, 120.4, 118.5, 112.0, 105.6, 103.2, 100.1, 61.7, 56.2, 55.9, 55.8. HRMS (EI^+, 70 eV) calcd for $C_{24}H_{18}Br_2O_4$ 527.9572, found 527.9562. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 2996, 2937, 2833, 1610, 1583, 1483, 1460, 1414, 1390.

4.9. Attempted synthesis of 2d

Compound **1d** was treated in an identical manner to that of **1a**. After extraction and concentration in vacuo, TLC and NMR of the crude product indicated that the desired product was not present.

4.10. 3,5,6,8,10,11-Hexamethoxybenzo[*j*]fluoranthene (2e)

Anhydrous ferric chloride (1.06 g, 6.41 mmol) was added portionwise to a stirred solution of 1,6,7-trimethoxynaphthalene (**1e**, 0.20 g, 0.92 mmol) dissolved in anhydrous DCM (5 mL) under argon. Upon completion of the addition the mixture turned deep red in colour and was stirred overnight at room temperature. The reaction mixture was cooled (0 °C, ice bath) and quenched with cold methanol (10 mL). The resultant mixture was extracted with DCM (2×20 mL), washed with 10% HCl (2×5 mL), dried ($MgSO_4$) and concentrated in vacuo. The product was purified by chromatography on silica gel eluting with DCM ($R_f \approx 0.30$) to afford a yellow/orange powder (0.13 g, 65%), which was recrystallized from $CHCl_3$/EtOH to afford the title compound as yellow prisms. Mp 231–232 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J=7.8 Hz, 1H), 7.80 (s, 1H), 7.62 (s, 1H), 7.61 (s, 1H), 7.43 (s, 1H), 6.83 (d, J=7.8 Hz, 1H), 4.14–4.06 (6×s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.4, 154.6, 154.3, 150.7, 148.8, 147.8, 134.9, 130.4, 127.6, 126.8, 126.5, 121.3, 121.1,

119.4, 105.5, 103.6, 102.6, 102.4, 100.9, 61.6, 56.6, 56.2, 56.2, 56.1; IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 3011, 2937, 2888, 2830, 1592, 1426, 1357. HRMS (EI^+, 70 eV); *m/z*: $[M]^+$ calcd for $C_{26}H_{24}O_6$ 432.1573, found 432.1570.

4.11. 4-Iodo-1,6-dimethoxynaphthalene (4)

N-Iodosuccinimide (5.57 g, 29.2 mmol) was added portionwise to a stirred solution of 1,6-dimethoxynaphthalene (5.00 g, 26.5 mmol) and trifluoroacetic acid (0.62 mL, cat. amount) dissolved in acetonitrile (125 mL). Upon completion of the addition the mixture turned dark brown. Stirring was continued for 2 h. Volatile organics were removed in vacuo and the resultant crude oil extracted with diethyl ether (100 mL). The organics were washed successively with satd $NaHCO_3$ (2×50 mL), water (2×50 mL), dried ($MgSO_4$) and concentrated in vacuo to afford a pale brown solid (6.50 g, 78%), which was recrystallized from EtOH. Mp 64 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J*=9.2 Hz, 1H), 7.90 (d, *J*=8.2 Hz, 1H), 7.32 (d, *J*=2.5 Hz, 1H), 7.12 (dd, *J*=9.2, 2.5 Hz, 1H), 6.47 (d, *J*=8.2 Hz, 1H). 3.97 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 155.5, 135.7, 130.3, 129.2, 124.2, 121.1, 117.5, 105.7, 102.12, 55.91, 55.90. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 2925, 2897, 2858, 1588, 1430, 1353. HRMS (EI^+, 70 eV); *m/z*: $[M]^+$ calcd for $C_{12}H_{11}IO_2$ 313.9798, found 313.9796. Anal. Calcd for $C_{12}H_{11}IO_2$: C, 45.88; H, 3.53; I, 40.40. Found: C, 46.00; H, 3.50; I, 40.30.

4.12. 2-(4,7-Dimethoxynaphthalen-1-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (5)

4-Iodo-1,6-dimethoxynaphthalene (**3**, 5.00 g, 15.9 mmol), pinacol borane (3.10 g, 23.8 mmol) and triethylamine (6.66 mL, 47.7 mmol) were dissolved in anhydrous dioxane (100 mL) and subsequently degassed with argon for 1 h. $PdCl_2$(dppf) (0.40 g, 4.7 mmol) was added to the mixture and degassed for a further 0.5 h. The mixture was brought to reflux with stirring for 3 h, allowed to cool and extracted with diethyl ether (100 mL). The organics were washed with water (2×50 mL), dried ($MgSO_4$) and concentrated in vacuo. The resultant crude oil was purified by chromatography on silica gel eluting with 50% DCM/hexane v/v to afford **5** as a pale orange oil (4.20 g, 84%), which crystallized on standing over a period of a few days. Mp 89–90 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.29–8.22 (m, 2H), 8.05 (d, *J*=7.8 Hz, 1H), 7.17 (dd, *J*=9.2, 2.5 Hz, 1H), 6.74 (d, *J*=7.8 Hz, 1H), 4.04 (s, 3H), 4.00 (s, 3H), 1.46 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8, 140.3, 138.0, 129.2, 123.9, 121.1, 120.8, 117.4, 117.1, 107.6, 105.7, 102.0, 101.6, 83.71, 55.8, 55.4, 25.44. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 3005, 2975, 288, 1621, 1581. HRMS (EI^+, 70 eV); *m/z*: $[M]^+$ calcd for $C_{18}H_{23}BO_4$ 314.1689, found 314.1680. Anal. Calcd for $C_{18}H_{23}BO_4$: C, 68.81; H, 7.38. Found: C, 68.55; H, 7.35.

4.13. 4,7,4′,7′-Tetramethoxy-[1,1′]binaphthalenyl (6)

A stirred solution of 4-iodo-1,6-dimethoxynaphthalene (1.56 g, 5.0 mmol), 2-(4,7-dimethoxy-naphthalen-1-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (1.72 g, 5.50 mmol) and barium hydroxide octahydrate (1.57 g, 5.50 mmol) dissolved in anhydrous dioxane (100 mL) was degassed with argon for 1 h. Tetrakis-triphenylphosphine (0.17 g, 0.15 mmol) was added under a fast stream of argon. The mixture was degassed for a further 0.5 h and brought to reflux for 16 h. The mixture was allowed to cool, extracted with chloroform (100 mL). The organic extracts were washed successively with water (2×30 mL), dried ($MgSO_4$) and concentrated in vacuo. The resultant crude was purified by column chromatography, eluting with 30% DCM/hexane v/v ($R_f \approx 0.40$) to afford a colourless powder (1.65 g, 89%), which was recrystallized from EtOH. Mp 198–200 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, *J*=9.2 Hz, 2H), 7.35 (d, *J*=7.8 Hz, 2H), 7.10 (dd, *J*=9.2, 2.5 Hz, 2H), 6.75 (d, *J*=7.9 Hz, 2H), 6.72 (d, *J*=2.5 Hz, 2H), 4.05 (s, 6H), 3.53 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 155.5, 135.7, 130.3, 129.2, 124.2, 121.1, 117.5, 105.7, 102.1, 55.9, 55.51. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 3008, 2937, 2831, 1615, 1585, 1450, 1426. HRMS (EI^+, 70 eV); *m/z*: $[M]^+$ calcd for $C_{24}H_{22}O_4$ 374.1513, found 374.1517.

4.14. 3,6-Dibromo-2,7-dihydroxynaphthalene (7)

Bromine (26.0 g, 0.162 mol) dissolved in acetic acid (50 mL) was added dropwise over a 20 min period to a stirred solution of 2,7-dihydroxynaphthalene (6.5 g, 0.046 mol) dissolved in acetic acid (150 mL). The mixture was diluted with water (20 mL) and brought to reflux. Upon discolouration of bromine, powdered tin (10 g, 0.084 mol) was added portionwise. The mixture was allowed to reflux for a further 4 h, allowed to cool to room temperature and diluted with water (100 mL), the precipitated product was filtered as a colourless solid (10.50 g, 72%), which was recrystallized from AcOH. Mp 188–190 °C (lit.[30] mp 186–190 °C). ^1H NMR (300 MHz, DMSO-d_6) δ 10.50 (s, 2H), 8.01 (s, 2H), 7.06 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 152.5, 134.3, 131.0, 124.4, 110.1, 108.4. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 3500–3300 (b), 2866, 2745, 1615, 1588, 1525. HRMS (EI^+, 70 eV); *m/z*: $[M]^+$ calcd for $C_{10}H_6Br_2O_2$ 315.8735, found 315.8741.

4.15. 3,6-Dibromo-2,7-dimethoxynaphthalene (8)

A solution of 3,6-dibromo-2,7-dihydroxynaphthalene (**7**, 3.00 g, 9.43 mmol), potassium carbonate (3.91 g, 28.3 mmol) and methyl iodide (1.71 mL, 28.3 mmol) dissolved in anhydrous acetone (100 mL) were stirred at room temperature under argon for 4 h. The reaction mixture was filtered through a Celite pad to remove the inorganics, which was washed with DCM (100 mL). The combined organic filtrate and washings were washed with 10% HCl (2×50 mL), water (2×50 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude solid was recrystallized from ethanol to afford the title compound as fine white needles (2.50 g, 77%), mp 177–178 °C (lit.[30] mp 176.5–178 °C). ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.05 (s, 2H), 3.98 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 133.9, 131.0, 125.3, 111.4, 105.7, 56.2; IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 2994, 2940, 2869, 2858, 1618, 1588, 1491, 1464. HRMS (EI^+, 70 eV); *m/z*: $[M]^+$ calcd for $C_{12}H_{10}Br_2O_2$ 343.9048, found 343.9059. Anal. Calcd for $C_{12}H_{10}Br_2O_2$: C, 41.65; H, 2.91; Br, 46.18. Found: C, 41.55; H, 2.85; Br, 46.05.

4.16. 2,3,6,7-Tetramethoxynaphthalene (9)

Sodium (0.21 g, 8.6 mmol) was added portionwise to anhydrous methanol (30 mL) stirred under an argon atmosphere. Upon complete dissolution, copper(I) iodide (1.65 g, 8.64 mmol), 3,6-dibromo-2,7-dimethoxynaphthalene (7, 1.50 g, 4.32 mmol) and anhydrous DMF (5 mL), were added to the reaction mixture and brought to reflux for 24 h. Additional copper(I) iodide (0.83 g, 4.32 mmol) and satd sodium methoxide (20 mL) were added to regenerate the catalyst and stirred at reflux for an additional 12 h. The reaction was quenched by the addition of water (10 mL) and extracted with DCM (2×25 mL), washed successively with 10% HCl (2×10 mL), water (2×10 mL), dried ($MgSO_4$) and concentrated in vacuo to afford a crude solid, which was recrystallized from ethanol to afford the title compound (0.75 g, 70%). Mp 255–256 °C (lit.[23] mp>200 °C). ^1H NMR (300 MHz, $CDCl_3$) δ 7.04 (s, 4H), 3.98 (s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 124.1, 55.8; IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 3064, 3003, 2964, 2937, 2887, 1669, 1608, 1528, 1510. HRMS (EI^+, 70 eV); *m/z*: $[M]^+$ calcd for $C_{14}H_{16}O_4$ 248.1049, found 248.1048.

4.17. 2,3,6,7-Tetrakis(hexyloxy)naphthalene (10)

2,3,6,7-Tetrahydroxynaphthalene was prepared freshly as required. A mixture of HBr (20 mL, 48%), tetrabutylammonium bromide (40 mg, 0.12 mmol) and zinc (ca. 200 mg) was brought to reflux (≈130 °C). 2,3,6,7-Tetramethoxynaphthalene (2.0 g, 8.1 mmol) was added in a single portion and stirred at reflux for 1 h. The reaction mixture was allowed to cool and diluted with water (20 mL) and filtered. The filtrate was concentrated in vacuo and resuspended in water (20 mL). The suspension was filtered, washed with water and dried over P_2O_5. The product was used in the next step without further purification. 2,3,6,7-Tetrahydroxynaphthalene (1.00 g, 5.20 mmol), potassium carbonate (5.74 g, 41.6 mmol), hexylbromide (6.96 g, 41.6 mmol) and potassium iodide (a few small crystals) dissolved in anhydrous DMF (20 mL) were stirred at 65 °C for 24 h under an argon atmosphere. The reaction was allowed to cool and was diluted with water, extracted with DCM (2×30 mL). The combined organic extracts were washed with water (2×20 mL), dried ($MgSO_4$) and concentrated in vacuo. The resultant crude product was chromatographed on silica gel eluting with 20% DCM/hexane v/v to afford a colourless solid (1.98 g, 72%), which was recrystallized from EtOH. Mp 118–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (s, 4H), 4.06 (t, J=6.6 Hz, 8H), 1.90–1.82 (m, 8H), 1.54–1.43 (m, 8H), 1.36–1.24 (m, 16H), 0.92 (t, J=6.7 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 124.4, 107.8, 69.0, 31.6, 29.2, 25.7, 22.6, 14.0; IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 2950, 2932, 2871, 2855, 1605, 1508, 1418. HRMS (EI^+, 70 eV); m/z: $[M]^+$ calcd for $C_{34}H_{56}O_4$ 528.4179, found 528.4189. Anal. Calcd for $C_{34}H_{56}O_4$: C, 77.22; H, 10.67. Found: C, 77.10; H, 10.80.

4.18. 1-Bromo-2,3,6,7-tetrakis(hexyloxy)naphthalene (11)

Bromine (453 mg, 146 μL, 2.85 mmol), was added dropwise to a cooled (0 °C, ice bath) stirred solution of 2,3,6,7-tetra(hexyloxy) naphthalene (**10**, 1.50 g, 2.85 mmol) dissolved in DCM (30 mL). The reaction mixture was allowed to warm to room temperature and stirred for a further 30 min. The mixture was diluted with DCM (70 mL), washed with satd $Na_2S_2O_3 \cdot 5H_2O$ (2×20 mL), water (2×30 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by chromatography on silica gel eluting with 20% DCM/hexane v/v to afford **11** as a colourless precipitate (0.52 g, 30%), mp 65–66 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (s, 1H), 6.99 (s, 2H), 4.15–4.02 (m, 8H), 1.94–1.82 (m, 8H), 1.55–1.45 (m, 8H), 1.37–1.30 (m, 16H), 0.95–0.89 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.0, 149.7, 149.3, 145.5, 127.0, 123.6, 115.5, 108.3, 107.9, 107.6, 73.9, 69.46, 69.44, 69.23, 32.1, 32.0, 31.9, 30.6, 29.6, 29.4, 26.2, 26.1, 26.1, 23.0, 23.0, 14.4, 14.0. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}); 2953, 2928, 2857, 1503, 1466, 1414. HRMS (EI^+, 70 eV); m/z: $[M]^+$ calcd for $C_{34}H_{55}BrO_4$ 606.3284, found 606.3289. Anal. Calcd for $C_{34}H_{55}BrO_4$: C, 67.20; H, 9.12; Br, 13.15. Found: C, 67.10; H, 9.20; Br, 13.15.

4.19. 1-(3′,4′-Bis(hexyloxy)phenyl)-2,3,6,7-tetrakis(hexyloxy) naphthalene (12)

Tetrakistriphenylphosphine (23 mg, 0.02 mmol) was added to a degassed mixture of ethylene glycol dimethyl ether (30 mL) and 2 M potassium carbonate (0.62 mL, 1.23 mmol) with stirring under an argon atmosphere. The reaction mixture was degassed for a further 0.5 h. 1-Bromo-2,3,6,7-tetrakis(hexyloxy)naphthalene (**11**, 250 mg, 0.41 mmol) and 2-(3,4-bis(hexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (332 mg, 0.83 mmol) were added under a fast stream of argon. The reaction mixture was stirred at 70 °C for 24 h. The reaction mixture was allowed to cool to room temperature, diluted with DCM (30 mL), washed with water (2×25 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by chromatography on silica gel eluting with 30% DCM/hexane v/v to afford **12** as a colourless solid (300 mg, 91%), which was recrystallized from EtOH. Mp 53–54 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03 (s, 2H), 6.98–6.93 (m, 2H), 6.90–6.87 (m, 2H), 4.10–4.04 (m, 4H), 3.96–3.92 (m, 2H), 3.84–3.81 (m, 2H), 3.79–3.66 (m, 4H), 1.89–1.68 (m, 12H), 1.54–1.28 (m, 36H), 0.92–0.80 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 148.9, 148.6, 148.0, 147.7, 129.2, 126.7, 123.2, 116.6, 113.3, 107.6, 106.5, 73.5, 69.3, 69.2, 69.0, 68.9, 68.3, 31.7, 31.6, 30.1, 29.4, 29.3, 29.1, 29.0, 25.9, 25.82, 25.7, 25.5, 22.6, 14.0, 14.0. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 2953, 2928, 2857, 1503, 1466, 1414. HRMS (EI^+, 70 eV); m/z: $[M]^+$ calcd for $C_{52}H_{84}O_6$ 804.6268, found 804.6265. Anal. Calcd for $C_{52}H_{84}O_6$: C, 77.56; H, 10.51. Found: C, 77.42, H, 10.22.

4.20. 3-Chloro-1,2,5,6,8,9-hexakis(hexyloxy)fluoranthene (13)

Anhydrous ferric chloride (120 mg, 0.18 mmol) was added portionwise to a stirred solution of 1-(3′,4′-bis(hexyloxy)phenyl)-2,3,6,7-tetrakis(hexyloxy)naphthalene (**12**, 150 mg, 0.75 mmol) dissolved in anhydrous DCM (5 mL) under an argon atmosphere. Upon completion of the addition the reaction mixture turned deep red in colour and was stirred overnight. The reaction mixture was cooled (0 °C, ice bath) and quenched with methanol (5 mL). The mixture was diluted with DCM (20 mL), washed with 10% HCl (2×10 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude product was subsequently realkylated with an excess of hexylbromide, potassium carbonate in DMF for 24 h at 65 °C. Upon completion of the reaction, the organics were extracted in DCM (2×30 mL), washed successively with 10% HCl (2×20 mL), water (2×20 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude was purified by chromatography on silica gel eluting with 40% DCM/hexane v/v to afford a yellow a waxy solid (104 mg, 67%), which was recrystallized from Me_2CO to afford the title compound a fine yellow needles. Mp 42 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.62 (s, 1H), 7.21 (s, 1H), 4.25–4.23 (m, 4H), 4.18–4.07 (m, 8H), 1.96–1.85 (m, 12H), 1.62–1.48 (m, 12H), 1.43–1.32 (m, 24H), 0.95–0.89 (m, 18H); IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 2950, 2928, 2857, 1604, 1571, 1487, 1463. HRMS (EI^+, 70 eV); m/z: $[M]^+$ calcd for $C_{52}H_{81}ClO_6$ 836.5722, found 836.5698. Anal. Calcd for $C_{52}H_{81}ClO_6$: C, 74.56; H, 9.75; Cl, 4.23. Found: C, 74.40; H, 9.60; Cl, 4.45.

4.21. 1,2,5,6,8,9-Hexakis(hexyloxy)fluoranthene (14)

A solution of 3-chloro-1,2,5,6,8,9-hexakis(hexyloxy)fluoranthene (**13**, 75 mg, 0.09 mmol) dissolved in anhydrous THF (5 mL) was degassed with argon for 0.5 h. Potassium fluoride (10 mg, 0.18 mmol) dissolved in water (1 mL) was added and the mixture degassed for a further 0.5 h. $Pd(OAc)_2$ (ca. 2 mg, 0.001 mmol) was added under a fast stream of argon. PMHS (63 μL, 0.38 mmol) was added and the mixture stirred at room temperature for 12 h. Upon completion of the reaction, unreacted PHMS was hydrolyzed with 3 M NaOH aq (5 mL). The reaction mixture was diluted with DCM (10 mL), washed with water (2×5 mL), dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by preparative TLC on silica eluting with 40% DCM/hexane v/v (R_f≈0.6) to afford **14** as a bright yellow powder (50 mg, 68%), which was recrystallized from (Me_2CO). Mp 33 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (s, 2H), 6.98 (s, 2H), 4.22 (t, J=6.6 Hz, 4H), 4.14–4.07 (m, 8H), 1.93–1.83 (m, 12H), 1.57–1.50 (m, 12H), 1.39–1.25 (m, 24H), 0.95–0.88 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9, 148.9, 144.6, 131.5, 110.5, 106.3, 74.5, 74.0, 69.7, 69.3, 31.84, 31.77, 31.65, 31.60, 30.8, 30.2, 29.4, 26.0, 25.9, 25.8, 22.6, 14.0; IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}) 2951, 2827, 2852, 1601, 1578, 1481, 1465. HRMS (ESI^+); m/z: $[M+Na]^+$ calcd for $C_{52}H_{82}O_6Na$ 825.6004, found 825.6015. Anal. Calcd for $C_{52}H_{82}O_6$: C, 77.76; H, 10.29. Found: C, 77.70; H, 10.25.

4.22. X-ray crystal structure of 3,6,8,11-tetramethoxybenzo[*j*] fluoranthene (2a)

Single crystals of compound **2a** were grown from $CHCl_3$/EtOH. X-ray diffraction measurements were carried out at 150 K on a Nonius KappaCCD diffractometer using graphite monochromated Mo Kα radiation. The structure was solved by direct methods with ShelXS[31] in the monoclinic space group $P2_1/n$ and was refined using SHELXL-97.[32] The asymmetric unit contains one molecule of **2a** and one molecule of chloroform, which was disordered over two positions with the ratio of the site occupation factors ultimately fixed at 0.70:0.30. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined using a riding model. C–H distances: methyl, 0.98 Å; aromatic, 0.95Å. All Uiso(H) values were constrained to be 1.2 times (1.5 for methyl) Ueq of the parent atom. At the conclusion of the refinement, the most extreme deviations in the residual electron density map are 1.40 at 0.6789, −0.0043, 0.1411 (0.91 Å from CL3S) and −1.43 at 0.7916, 0.0947, 0.1780 (0.80 Å from CL3S).

Crystal Data for compound **2a** (M=491.77): monoclinic, space group $P2_1/n$ (no. 14), a=7.5360(1) Å, b=12.1427(2) Å, c=24.3735(4) Å, β=92.608(1)°, V=2228.05(6) Å^3, Z=4, T=150(2) K, μ(Mo Kα)=0.442 mm^{-1}, D_{calcd}=1.466 g/mm^3, 22,614 reflections measured ($6.04 \leq 2\Theta \leq 52$), 4355 unique ($R_{int}$=0.0740), which were used in all calculations. The final $R1$ was 0.0571 ($>2\sigma(I)$) and $wR2$ was 0.1499 (all data). CCDC number 967582.

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Supplementary data

Crystallographic characterization for **2a** (CIF). ^{1}H NMR and ^{13}C {^{1}H} spectra for compounds **1b**–**14**. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.11.029.

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